Frequency up-conversion as a temperature probe of organic opto-electronic devices

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Frequency up-conversion is demonstrated in a polyfluorene-based conjugated polymer. Up-converted emission is observed upon excitation to the red of the 0-0 luminescence band. The emission intensity depends strongly on temperature and provides an accurate probe of the operating temperature of organic light-emitting diodes. Temperature rises of up to 30 K are observed at standard operating current densities of 225 mA/cm^2. Due to the low thermal conductivity and heat capacity of the polymer film, the temperature of the film is found to rise slowly on a time-scale of seconds. Upon termination of the current, the temperature decreases again on a time-scale of minutes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1432766]

Phonon mediated frequency up-conversion is an interesting phenomenon intrinsic to luminescent materials. Upon excitation at the lower energy side of an emission band, a phonon can combine with the incident photon in the anti-Stokes process to yield an excitation higher in energy than the incident photon. This process has previously been observed in organic materials, and has even led to the demonstration of laser cooling in the condensed phase.[1] As was pointed out by Clark and Rumbles,[1] anti-Stokes luminescence provides an accurate noninvasive measure of the temperature of the sample. Surprisingly, to date little interest has been shown in the anti-Stokes excitation process in conjugated polymers. Highly fluorescent conjugated polymers have been used in a variety of applications, most notably light-emitting diodes (LEDs)[2] and field effect transistors.[3] In these devices, ohmic current heating of the electrically active layer is invariably a problem due to the low intrinsic mobilities.

Heating effects are expected to become particularly problematic in LEDs at high excitation densities, for example, in passive matrix display elements, as was recently discussed by Wilkinson *et al.*[4] Also, electrically driven polymer lasing will, if at all, only be possible with suitable thermal management. Despite the awareness of the problems in terms of operation efficiency and stability introduced by heating, there have only been a few attempts to infer the operating temperature of an LED. In the first instance, Tessler *et al.* monitored the change in the electroluminescence (EL) spectrum and associated the blueshift with increasing current density with a film temperature rise of up to 60 K.[5] Zhou *et al.* used thermal imaging to estimate the temperature of Alq_3 based LEDs.[6] However, in this case the infrared radiation transmitted through the indium tin oxide (ITO) coated glass substrate was recorded, which may differ substantially from the actual temperature of the organic film.

In this letter, anti-Stokes luminescence is demonstrated as a direct and accurate, yet simple, measure of the polymer temperature. Frequency up-conversion was observed in toluene solutions (10 μg/ml) of the polymer poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PF2/6) upon excitation to the red of the 0-0 emission band with a tunable frequency doubled mode locked titanium sapphire laser operating at an average power of 1 mW. The sample was mounted in a cylindrical cuvette in a continuous flow helium cryostat and the spectra were recorded with a charge coupled device detector coupled to a 0.3 m monochromator equipped with a 300 lines/mm grating. Figure 1 shows the photoluminescence (PL) spectra excited at 430 nm and recorded at different temperatures. At room temperature, emission to the blue of the laser peak is observed and the characteristic vibronic bands of the PF2/6 emission are seen. As the temperature is reduced, the PL intensity decreases strongly, until it is barely detectable at 190 K. The inset in Fig. 1 shows the intensity of the 0-1 band at 445 nm as a function of inverse temperature. The spectra are evidently thermally activated with an activation energy of 0.11 eV. The PL spectrum with excitation at 390 nm is also

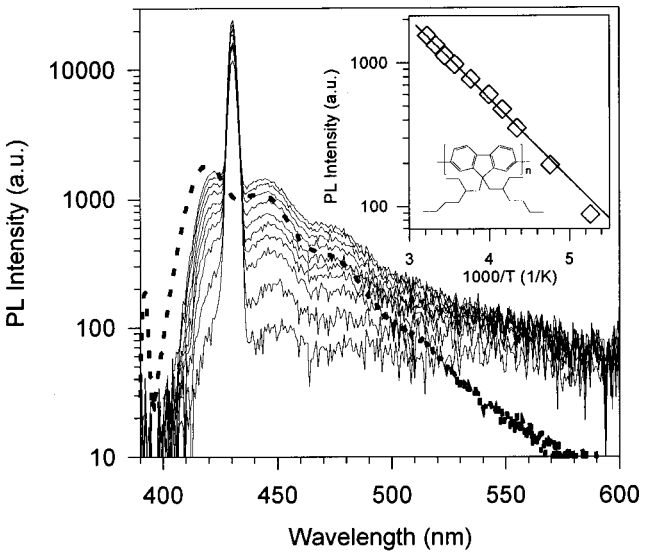

FIG. 1. Temperature dependence of fluorescence up-conversion in a solution of the polyfluorene derivative (PF2/6). The spectra were recorded at 310, 300, 290, 280, 265, 250, 240, 230, 210, and 190 K (from top to bottom). The dotted curve shows the solution emission spectrum upon excitation at 390 nm. The inset shows the thermal activation of the 0-1 band intensity of the emission spectrum. The chemical structure of PF2/6 is also given.

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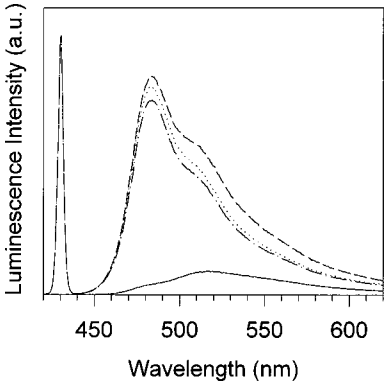

FIG. 2. Emission spectra of a PF2/6 LED studied through a 455 nm long-pass filter. The solid line shows the EL spectrum, the PL spectrum of the LED in the off-state is shown by the dash-dotted line and the PL spectrum of the LED in the on-state is indicated by the dashed line. The dotted spectrum corresponds to the difference between on-state PL spectrum and EL spectrum.

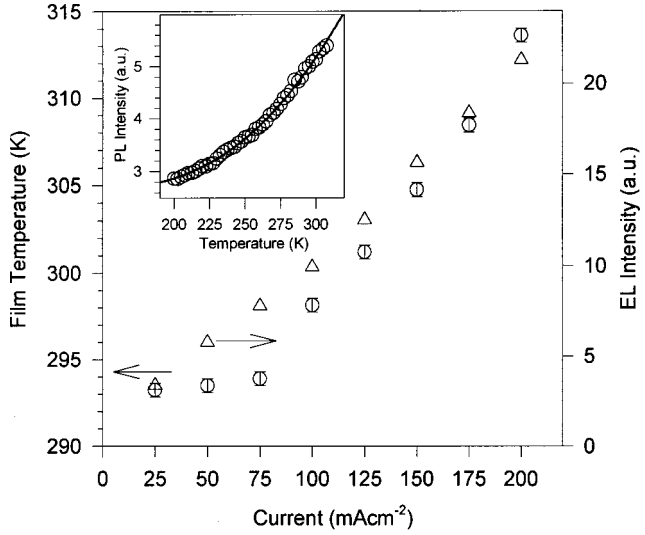

FIG. 3. Measured brightness (triangles) and polymer film temperature (circles) for different current densities. The inset shows the change of the anti-Stokes PL intensity (integrated from 460 to 600 nm) with temperature and the corresponding fit, taking into account a nonactivated absorption component due to aggregation.

shown in the figure for comparison (dotted line). The emission band origin appears to be shifted slightly to the blue and the 0-0 emission band at 420 nm is more pronounced. The vibronic modes, however, are observed at the same wavelengths. This slight difference between the Stokes and anti-Stokes spectra may be a result of probing only segments with longer conjugation in the case of anti-Stokes excitation and will be investigated in a future publication.

In order to observe frequency up-conversion in films, a 455 nm long-pass filter had to be placed in front of the spectrometer. This is because the luminescence yield is reduced somewhat in comparison to solution, and the backscattered laser light is dramatically enhanced, particularly by the presence of metallic electrodes. In order to study current heating in LEDs, single layer LEDs were fabricated on ITO substrates coated with a 50 nm hole injecting layer of polyethylenedioxythiophene doped with poly(styrene sulfonate) and contacted with calcium electrodes (15 nm) covered by aluminum (150 nm). The active area of the LED was 4 mm^2. The LEDs were contacted and mounted under vacuum in a cryostat. The laser beam was focused down to a diameter of 100 μm onto the active area of the LED. The LEDs were driven by a source measure unit in constant current mode. The phonon assisted PL emission from the LED pixel is shown in Fig. 2. It is found to increase substantially upon application of a current of 5 mA (125 mA/cm^2 at approx. 6 V). The solid line in Fig. 2 shows the electroluminescence (EL) spectrum recorded. As commonly observed,[7–10] there is a strong emission band at approx. 520 nm associated with the formation of defects in the film, which appear to be more prevalent in EL than in PL. The dotted line shows the difference between the PL spectrum measured during operation and the EL spectrum. The difference spectrum is still significantly more intense than the unbiased PL spectrum, particularly in the higher energy region. This is all the more surprising, since previous experiments on the PL of LED structures revealed a reduction in luminescence due to field induced exciton dissociation[11] or polaron quenching.[12]

Polyfluorenes are known to form aggregates in the solid state,[13–14] which will result in additional absorption in the anti-Stokes region of excitation. It has been shown that highly ordered and extended polymer chains can result in a new absorption feature to the red of the π-π^* absorption band. In particular, thermal annealing, which is of relevance to LEDs as it may occur during operation, was shown to result in the appearance of a low energy absorption shoulder.[14] This means that, in contrast to solutions, films may be excited to the red of the 0-0 transition even in the absence of phonons. This may, however, result in a change of emission spectrum, as the aggregate emission band generally exhibits redshifted features. The additional absorption may be taken account of to a first approximation by assuming a constant, temperature independent emission contribution to the temperature dependent PL. This is shown in the inset of Fig. 3. As for the case of the solution PL, the PL of the LED pixel exhibits an exponential activation of the form $PL(T) = PL_0 + A^* e^{-\Delta E/kT}$, where PL_0 is the approximately temperature independent PL due to aggregate absorption and A is a constant. Although it is conceivable that the luminescence resulting from aggregate absorption is most likely temperature dependent itself, the temperature dependence of this feature is expected to be much weaker than the exponential activation of anti-Stokes luminescence. The PL intensity of the LED pixel is found to halve between 310 and 200 K. It is conceivable that the film luminescence intensity generated by direct absorption of a photon could both increase with decreasing temperature due to a reduction in nonradiative decay channels, but also decrease with decreasing temperature due to increased quenching of singlet excitons by polarons preferentially trapped on the aggregate states. It is, therefore, instructive to compare the temperature dependencies of both film and solution luminescence. A comparison of the activation energies for film and solution yields values of 0.12 ± 0.01 and 0.11 ± 0.01 eV, respectively, in good agreement with each other. It may hence be concluded that in the film the bulk of the temperature dependence of the PL intensity over the temperature range studied arises from the anti-Stokes process rather than from a change in magnitude of emission from aggregate states, as there is no aggregate absorption in the case of solutions. The percentage of the

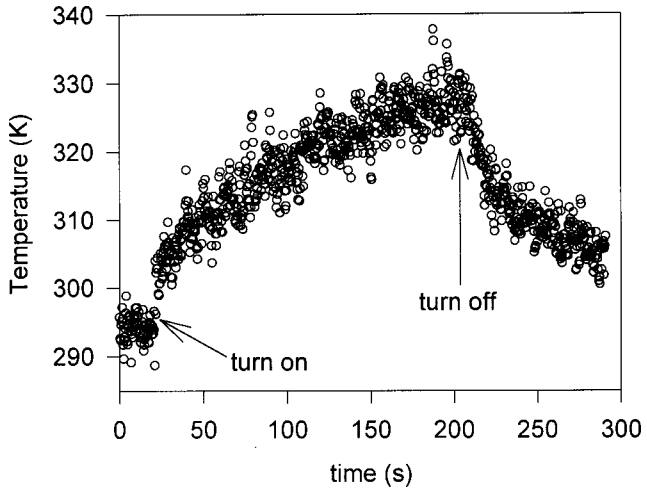

FIG. 4. Temporal evolution of the polymer film temperature at a current density of 225 mA cm^{-2}.

change of PL intensity upon operation of the LED can hence be used to infer the operating temperature. This is demonstrated in Fig. 3, where the EL intensity and the calculated temperature are plotted. The temperature was deduced by correcting the anti-Stokes PL spectrum of the operating LED for the emitted EL intensity, as shown in Fig. 2. Above a current density of 75 mA/cm^2 the LED temperature is found to increase. For standard continuous wave (cw) operating conditions of the LED, a significant rise of the film temperature is observed. Above 200 mA/cm^2 a steady state value for the temperature was not reached, indicating a positive feedback between the injected current density, the operating temperature and the conduction mechanism (the mobility), which in turn depends on temperature.

Due to the low thermal conductivity of the polymer film, both heating and particularly cooling are very slow processes. Whereas the EL turn-on and turn-off dynamics occur on the time-scale of microseconds, heating and cooling are found to occur on time-scales of seconds to minutes. This surprising result is depicted in Fig. 4, where the film temperature is shown as a function of time. Upon application of a constant current (225 mA/cm^2) to the device, there is an initial sharp increase in temperature by approx. 8 K followed by a more gradual rise of 20 K over 3 min. Upon turning off the current flow an initial cooling by 10 K is observed over the first 10 s, followed by a much slower reduction in temperature and hence PL intensity. This remarkable observation complements the studies by Tessler *et al.*[5] on the use of different heat sinks on LEDs and shows that heat storage in the polymer film is indeed a serious problem. However, as the anti-Stokes probe is much more sensitive than a direct measurement of the change of the emission spectrum, this technique also allows fundamental insights to be made into the nature of heat transport in these thin thermally insulating films. In view of the current debate on the influence of film morphology on the charge transport and emission properties (e.g. Ref. 15), it will be a particularly interesting field of research to correlate the thermal transport properties with morphology.

In summary, fluorescence up-conversion has been demonstrated in a conjugated polymer. This is shown to provide an accurate probe of the operating temperature of the active layer of a polymer LED. Temperature rises of up to 30 K are observed under cw operation. The new technique is of importance for the characterization of passive matrix display elements as well as for the development of polymer laser diodes.

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